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GALLIUM ARSENIDE MATERIALS GROWTH AND PROCESSING.(U)
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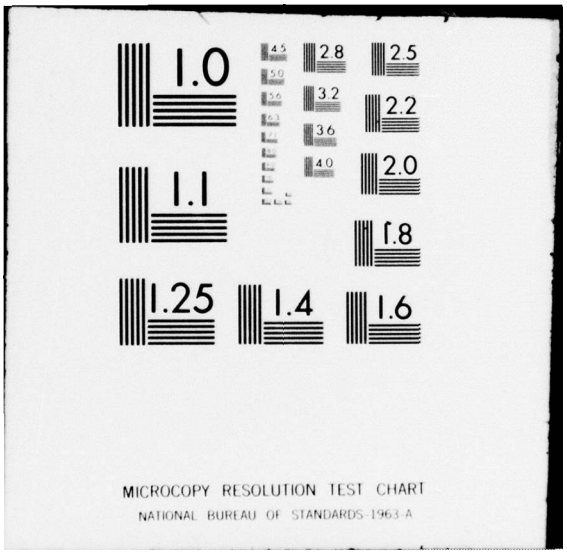
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By

(10) D. W. Shaw

Texas Instruments Incorporated
Central Research Laboratories
13500 North Central Expressway
P. O. Box 5936
Dallas, Texas 75222

(16) 2306 (17) B1

(18) AFOSR (19) TR-78-1170

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SECTION I
PROGRAM OBJECTIVES

Gallium arsenide solid-state microwave devices are currently in a stage of rapid development. These advanced devices are being exploited to extend the performance levels of several key microwave systems of military importance. Currently, the capabilities of these devices are limited by the quality of the epitaxial material within which they are fabricated and by the ability to process this material into precisely defined device geometries. As the devices are applied to higher and higher frequencies, the requirements placed on the epitaxial layers, particularly with respect to thickness control, and on the fineness of the device geometries place severe demands on the epitaxial growth and processing procedures. It has been recognized that solid state diffusion of incorporated dopant can limit the widths of compositional transitions and hence the ultimate layer thicknesses in multilayer epitaxial structures. Since the rates of solid state diffusion decrease significantly with decreasing temperatures, it should be possible to reduce the diffusion limitations by epitaxially growing the structures at lower temperatures. However, epitaxial growth is a complex process sensitive to many parameters, and to achieve reliable growth at subnormal temperatures, special growth procedures must be developed. Establishment of such procedures was the primary objective during the initial phase of the program. The relative significances of the thermodynamic and kinetic factors in determining the minimum temperature for epitaxial growth of gallium arsenide by chemical vapor deposition were to be assessed, and, as a result, the optimum conditions for growth of gallium arsenide layers at the lowest practical temperatures were to be defined.

The next phase of the program emphasized evaluation of complex epitaxial structures grown at low temperatures under the conditions established during the initial phase. This evaluation included not only a comparison of the physical and electrical characteristics of epitaxial structures grown at low

and conventional temperatures, but also fabrication of microwave devices from material deposited under low temperature conditions.

Advanced devices require not only thinner epitaxial layers, but also greatly reduced device geometries. Consequently, considerable effort is being expended in the U. S. and abroad to develop microdefinition procedures such as e-beam and x-ray lithography. Yet, the crucial chemical etching steps available for use in processing these structures are, in general, empirically developed processes. During the last phase of the program, the objective was to advance the state-of-the-art in GaAs etching technology. Particular emphasis was to be placed on theoretical and experimental characterization of etch rate anisotropy with respect to crystallographic orientation. Various etchant compositions were to be systematically investigated and classified with respect to the shape of the resulting etched profiles. Such information is essential for improvement of existing gallium arsenide device processing procedures and for development of new and improved device designs.

The specific objectives of the program are listed below.

- Perform iterative computer calculations of gas phase supersaturation as a function of temperature and vapor composition for GaAs epitaxial deposition with a $Ga/AsCl_3/H_2$ system.
- Determine the critical temperature for onset of extraneous nucleation and nonselective deposition as a function of the vapor composition in this growth system.
- Measure, by means of an <u>in situ</u> recording electro-balance, the GaAs epitaxial growth kinetics as a function of vapor composition to determine the optimum conditions for low temperature epitaxial growth.
- Determine the degree of correlation between the conditions experimentally established for low temperature deposition and the computed gas phase supersaturation.

- Evaluate the influence of substrate crystal perfection on the conditions required for low temperature deposition.

- Compare, using interference contrast microscopy, the relative crystal perfection of layers grown at low and normal deposition temperatures in the *in situ* rate monitoring apparatus.

- Extend this comparison of perfection to layers grown at low and normal temperatures in a conventional GaAs epitaxial growth system.

- Grow complex GaAs epitaxial structures at conventional and at subnormal temperatures.

- Compare the physical and electrical properties of complex GaAs epitaxial structures grown at conventional and at subnormal temperatures.

- Examine the relative abruptnesses of doping level transitions as a function of growth temperature.

- Evaluate growth of buffer layers suitable for GaAs FET structures. Assess the feasibility of growth of these buffer layers at subnormal temperatures.

- Characterize the electrical properties of the grown layers by use of capacitance-voltage and/or Hall effect measurements.

- Evaluate the properties of GaAs layers epitaxially grown at subnormal temperatures on germanium substrates.

- Evaluate the characteristics of microwave devices fabricated in GaAs epitaxial layers grown at subnormal temperatures.

- Systematically evaluate and classify the characteristics of GaAs liquid etchants.

- Relate these characteristics to the fundamental rate limitations encountered in chemical etching.

- Assess the orientation dependencies of the etchants and assimilate the results in a manner appropriate for selection of the proper etchant composition to produce a desired etch shape or profile.

SECTION II
SUMMARY OF ACCOMPLISHMENTS

The minimum temperature for epitaxial growth with CVD systems is determined by a combination of thermodynamic and kinetic factors. In general, the kinetic factors (such as the chemical surface reactions) result in lower deposition rates as the deposition temperature is reduced until, finally, a point is reached such that the deposition rate is vanishingly small. The thermodynamic factors may aid or inhibit low temperature deposition, depending on the sign of the enthalpy (ΔH) for the overall process. The well-known $Ga/AsCl_3/H_2$ process for deposition of epitaxial GaAs for microwave devices is an exothermic process (ΔH negative), and reduction of the deposition temperature under otherwise constant conditions results in an increased gas phase supersaturation or chemical potential for deposition. However, this is also accompanied by a decrease in the rate of the chemical surface processes leading to epitaxial growth. As the latter events actually determine the epitaxial growth rate, continued reduction in the growth temperature should simply result in successively lower deposition rates.

From the activation energy of the rate-limiting surface event, one should, in principle, be able to predict the minimum temperature for CVD epitaxial growth by extrapolation from the normal-temperature growth rates. In practice, this is complicated by the onset of heterogeneous nucleation and extraneous deposition of gallium arsenide on the fused silica reactor tube and substrate holder. At normal temperatures the supersaturation is sufficiently low that heterogeneous nucleation is prevented and growth is essentially limited to the substrate. However, since the gas phase supersaturation increases with decreasing temperature, heterogeneous nucleation becomes increasingly probable at low temperatures. The extraneous gallium arsenide deposits formed by heterogeneous nucleation on the surrounding fused silica reactor parts compete with the substrate for reactants and effectively lower the reactant partial

pressures near the substrate surface. Hence, at low temperatures epitaxial growth rates may be severely reduced below the expected values if significant heterogeneous nucleation occurs. The optimum conditions for low temperature epitaxial growth are those which permit reasonable epitaxial growth rates with minimal heterogeneous nucleation. These conditions were established during the first phase of the program.

In growth of a compound semiconductor by chemical vapor deposition techniques the gas phase supersaturation may be controlled in a number of ways. Iterative computer calculations demonstrated the effects of the inlet gas composition, source temperature, and substrate temperature on the gas phase supersaturation in GaAs depositions. The results of these calculations provided guidance for the experimental kinetic measurements that followed. These measurements were obtained on an in situ, continuous rate monitoring apparatus. With this apparatus the growing gallium arsenide crystal is suspended by means of a fine fused silica fiber from one arm of an electronic microbalance. By electronically differentiating the balance output signal with respect to time, the deposition (or etch) rate was continuously monitored. The experimental approach permitted not only measurement of the epitaxial growth rate as a function of the gas phase supersaturation, but also detection of the temperature at which heterogeneous nucleation of extraneous GaAs on the silica fiber began.

Prior to these kinetic studies it was expected that low temperature deposition would ideally be obtained by decreasing the overall gas phase supersaturation. Addition of a small amount of "excess" $AsCl_3$ to the gas stream leaving the Ga source was demonstrated by equilibrium calculations to be an effective method of supersaturation reduction. Experimentally, however, it was found that heterogeneous nucleation of GaAs on fused silica is not a simple function of the gas phase supersaturation as predicted by classical heterogeneous nucleation theories. While of obvious scientific importance, this

conclusion did not solve the immediate practical problem of achieving selective epitaxial growth at low temperatures. Extensive kinetic analyses were conducted as a function of the extent of source dilution, source temperature, arsenic partial pressure, and the gallium monochloride partial pressure. The results of these analyses led to the conclusion that the reduction of the partial pressures of the source reactants is the only effective means of achieving very low temperature selective deposition. As a result of these efforts, conditions were established for growth of epitaxial GaAs layers at temperatures as low as 575°C (compared to the ~750°C temperature generally employed).

During the second phase of the program, the operation of a classic Ga/$AsCl_3/H_2$ growth system at deposition temperatures down to 550°C was subjected to a detailed evaluation. The same growth system was employed for deposition at both conventional and subnormal temperatures to permit comparison of the properties of layers deposited under both conditions. Numerous epitaxial structures of varying degrees of complexity were grown at temperatures ranging from the conventional 750°C down to 550°C during this phase. Initially, all layers grown at subnormal temperatures were deposited on an epitaxial buffer layer grown at 750°C during the same run. Later, however, techniques were developed for growth at low temperatures directly on the substrate.

The surfaces of wafers deposited at temperatures down to as low as 575°C were unexpectedly bright and free of visible defects, particularly when the low temperature layers are sequentially deposited on a buffer layer. It should be stressed, however, that such good layers were obtained only with special care when deposited at subnormal temperatures. In general, deposition at subnormal temperatures is less reproducible than normal temperature growth and requires greater attention to surface preparation and leak control for successful layers.

In general, it was found that the most important factors for successful growth at subnormal temperatures are (1) careful elimination of small leaks in the gas handling system, (2) the use of sources with limited surface area to minimize the source reactant concentrations in the deposition zone while maintaining source saturation, (3) high flow velocities in the deposition zone, and (4) scrupulous care in substrate surface preparation. The reproducibility from run to run is improved considerably by use of a single crystal GaAs solid source instead of the usual arsenic-saturated liquid gallium source. However, even with solid sources, small surface areas are desirable to minimize extraneous deposition. Good surface morphologies were obtained at temperatures below 600°C even without the use of a buffer layer deposited at conventional temperatures. Under optimum conditions little degradation in interfacial perfection is observed on the etched cross sections of layers grown at subnormal temperatures. Likewise, the electrical characteristics of layers deposited at subnormal temperatures were similar to those of layers grown under conventional conditions in the same apparatus. In one case a layer grown at 595°C had a room temperature mobility of 8,000 $cm^2\ V^{-1}\ s^{-1}$ for a carrier concentration of $4.3 \times 10^{14}\ cm^{-3}$. The mobility of this layer exceeded 60,000 $cm^2\ V^{-1}\ s^{-1}$ at 77 K. Detailed measurements of doping profiles in multilayer structures demonstrated that significant improvements in the abruptness of doping level transitions can be achieved by growth at subnormal temperatures.

It was concluded that device-quality epitaxial GaAs could be deposited at temperatures below 600°C. Additional experiments revealed that heteroepitaxial GaAs layers could also be grown on Ge substrates at such temperatures, thus minimizing the extent of solid state interdiffusion that occurs across the GaAs/Ge interface.

Gallium arsenide precision and orientation-dependent etching technology was significantly advanced during the final phase of the program. A special photomask was designed and implemented to provide data on etch rate, surface

morphology, and azimuthal and cross-sectional anisotropy. Acidic and alkaline hydrogen peroxide based etchants were systematically investigated. In addition, a number of miscellaneous compositions including halogen-alcohol, potassium ferricyanide, and ceric sulfate based etchants were studied.

Both isotropic, mass-transport-limited and highly anisotropic, kinetically limited compositions were identified. Certain bromine-methanol compositions were found to be extremely orientation-dependent and to exhibit "zero undercutting" characteristics. The latter feature should be particularly important in advanced device fabrication. A wide variety of cross-sectional profiles may be achieved in formation of GaAs mesas or channels through chemical etching. Suitable compositions for producing acute, obtuse, smoothly curved, and combination wall profile angles were identified.

Particular attention was given to the hydrogen peroxide based etchant compositions. With the $H_2SO_4/H_2O_2/H_2O$ system the etch rates for the more dilute compositions exhibit a linear (first-order) dependence on the H_2O_2 concentration; however, the rate is enhanced as the H_2SO_4/H_2O ratio approaches unity. A notable feature of $NaOH/H_2O_2$ etchants is that very shallow wall slopes can be obtained in certain crystallographic directions when the $NaOH:H_2O_2$ ratio is relatively high.

A procedure was developed to permit graphic analysis of the cross-sectional profiles produced by localized etching. Starting with the cross-sectional profiles measured on orthogonal cleaved cross sections through {001} GaAs slices, the profiles for slices of other orientations can be predicted and graphically displayed. This new approach is expected to be very beneficial in optimizing device and circuit design to take advantage of orientation-dependent etching or other special anisotropic etching properties.

SECTION III

LIST OF PUBLICATIONS

1. D. W. Shaw, "Gas Phase Composition and Extraneous Deposition in GaAs Vapor Phase Epitaxy," J. Crystal Growth 35, 1 (1976).

2. D. W. Shaw, "GaAs Vapor Phase Epitaxy at Subnormal Temperatures," Electrochemical Society Extended Abstracts 77-2, 862 (1977).

3. D. W. Shaw, "Morphology Analysis in Localized Crystal Growth and Dissolution,"* (in preparation).

4. D. W. Shaw, "Localized GaAs Dissolution. I. Acidic Hydrogen Peroxide Based Etchants,"* (in preparation).

5. D. W. Shaw, "Localized GaAs Dissolution. II. Alkaline Hydrogen Peroxide and Bromine-Methanol Based Etchants,"* (in preparation).

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* Tentative Titles

SECTION IV

LIST OF ORAL PRESENTATIONS

1. D. W. Shaw, "Gas Phase Supersaturation and Heterogeneous Nucleation in GaAs Vapor Deposition," Third Annual Conference on Crystal Growth, July 1975, Stanford University.

2. D. W. Shaw, "GaAs Vapor Epitaxy at Subnormal Temperatures," Fall Meeting of the Electrochemical Society, October 1977, Atlanta, Georgia.

3. D. W. Shaw, "Localized GaAs Dissolution. I. Acidic Hydrogen Peroxide Based Etchants," tentative title, anticipated presentation.

4. D. W. Shaw "Localized GaAs Dissolution. II. Alkaline Hydrogen Peroxide and Bromine-Methanol Based Etchants," tentative title, anticipated presentation.

SECTION V
ADMINISTRATIVE

Don W. Shaw served as both program manager and principal investigator during the program. No consultations with Department of Defense Laboratories were conducted, and no patents or patent disclosures were originated as a result of the activities.

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Continuous, in situ rate measurements were employed to evaluate the influence of gas phase supersaturation on the gallium arsenide epitaxial growth kinetics relative to the extent of heterogeneous nucleation and extraneous deposition on fused silica. The resulting kinetic data permit establishment of the optimum conditions for selective epitaxial growth of gallium arsenide at subnormal temperatures using the classic gallium/arsenic trichloride/hydrogen chemical vapor deposition process. Specifically, the extent of extraneous

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deposition is minimized through the use of low arsenic partial pressures entering the source region or through the use of small source surface areas. Using the identified conditions, vapor phase growth of gallium arsenide layers at temperatures below 600°C were achieved. Layers with good surface morphologies were obtained at temperatures down to 575°C. Under optimum conditions, the layers grown at subnormal temperatures exhibited little degradation in electrical properties as compared with those of layers grown in the same apparatus at conventional temperatures (750°C). For example, a layer grown at 595°C had a carrier concentration of 4.3×10^{14} cm^{-3} with an associated mobility of 8,000 $cm^2 V^{-1} s^{-1}$ at 300 K. At 77 K the mobility exceeded 60,000 $cm^2 V^{-1} s^{-1}$. Detailed measurements of doping profiles in multilayer structures demonstrated that significant improvements in the relative abruptnesses of doping level transitions can be obtained by growth at subnormal temperatures.

The kinetics and cross-sectional etch morphologies produced by various gallium arsenide etchants were systematically investigated. Both isotropic and highly anisotropic compositions were identified. A procedure was developed for graphic analysis of the cross-sectional profiles produced in localized or selective etching. The procedure permits prediction of the locally etched cross-sectional profiles for various substrate orientation on the basis of the results measured on locally etched {001} slices.